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LETTERS TO THE EDITOR

Formation of the P–C and C–C bonds in the Reaction of 2-(5-Methyl-2-phenyl-2*H*-1,2,3-diazaphosphol-4-yl)-4*H*-benzo[*e*]-1,3,2-dioxaphosphorin-4-one with Dimethyl Acetylenedicarboxylate under Mild Conditions[1]

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Abstract—2-(5-Methyl-2-phenyl-2*H*-1,2,3-diazaphosphol-4-yl)-4*H*-benzo[*e*]-1,3,2-dioxaphosphorin-4-one reacts under mild conditions with dimethyl acetylenedicarboxylate with the participation by only three-coordinated phosphorus atom and the formation of 2-(5-methyl-2-phenyl-2*H*-1,2,3-diazaphosphol-4-yl)-3,4-dimethoxycarbonylbenzo[*f*]-1,2-oxaphosphepine-2,5-dione. During the process, simultaneous formation of the P–C and C–C bonds takes place.

Keywords: diazaphosphol, dioxaphosphorine, dimethyl acetylenedicarboxylate, benzooxaphosphepine

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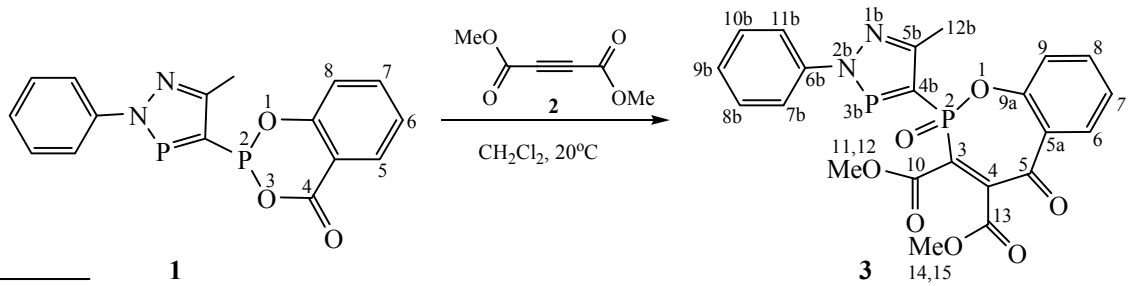
The 4*H*-benzo[*e*]-1,3,2-dioxaphosphorin-4-one derivatives containing the highly reactive P–OC(O) fragment easily enter the six-membered ring extpansion reactions (to seven-membered ring) effected by activated carbonyl compounds [1] and benzylidene derivatives of malonic ester [2, 3]. The introduction of a weakly acceptor and bulky 5-methyl-2-phenyl-2*H*-1,2,3-diazaphosphol-4-yl substituent to the phosphorus atom enhances the tendency to expand the ring under the influence of unsaturated systems. as shown by the example of the reactions of 2-(5-methyl-2-phenyl-2*H*-1,2,3-diazaphosphol-4-yl)-4*H*-benzo[*e*]-1,3,2-dioxaphosphorin-4-one **1** with hexafluoroacetone, methyl trifluoropyruvate, and diethyl ester of mesoxalic acid [4–7]. In this case, the diazophospholyl substituent does not participate in the reaction.

Here we report for the first time on a possibility of compound **1** to enter into the ring extpansion reaction at the action of dimethyl acetylenedicarboxylate **2** with the simultaneous formation of the P–C and C–C bonds. The process was carried out in dichloromethane under mild conditions and did not affect the fragment with a two-coordinated phosphorus atom (Scheme 1).

The resulting oxaphosphepine **3**, a thick pale yellow oil, was characterized by mass, IR, and NMR spectra. Thus, in the mass spectrum (EI) there was a peak of a molecular ion with *m*/*z* 484. The $^{31}P\{^{1}H\}$

Scheme 1.



[1] Supporting materials are available from authors.